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We have used the scanning tunneling microscope (STM) to move adsorbates such as benzene molecules and Xe clusters in order to determine their initial adsorption site. This has allowed us to image the initiation of the growth of a Xe surface overlayer, and to identify the sites at which this growth begins. This capability has also allowed us not only to examine the binding sites of the adsorbates, but also to learn the effect that these sites have on the STM images.

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What is Underneath? Moving Atoms and Molecules to Find Out

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WHAT IS UNDERNEATH? MOVING ATOMS AND MOLECULES TO FIND OUT

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We have used the scanning tunneling microscope (STM) to move adsorbates such as benzene molecules and Xe clusters in order to determine their initial adsorption site. This has allowed us to image the initiation of the growth of a Xe surface overlayer, and to identify the sites at which this growth begins. This capability has also allowed us not only to examine the binding sites of the adsorbates, but also to learn the effect that these sites have on the STM images.

1. Introduction

Special surface sites such as steps and defects are thought to play an important and often dominant role in surface chemistry and in other surface processes such as diffusion [1]. We have previously shown how Xe atoms at dilute coverage first fill adsorption sites adjacent to steps, then form clusters on the terraces of the Pt{111} surface [2]. Using the STM tip to move the clusters allows subsequent imaging of the substrate sites at which the cluster islands nucleated and grew. In addition, we have shown how the appearance of an adsorbate in an STM image can vary according to binding site [3,4]. While this provides useful information on how electronic structure varies according to chemical environment, it also places constraints on the use of the STM in identifying molecules on surfaces. Moving the adsorbates once again allows examination of the initial binding sites.

2. Experimental

The experiments described here were conducted with an ultrahigh vacuum (UHV) scanning tunneling microscope at 4K. This microscope is equipped with a room temperature ultrahigh vacuum preparation and analysis chamber and a load lock. A schematic of the instrument is shown in Fig. 1. The STM is housed in a UHV chamber which itself is in an

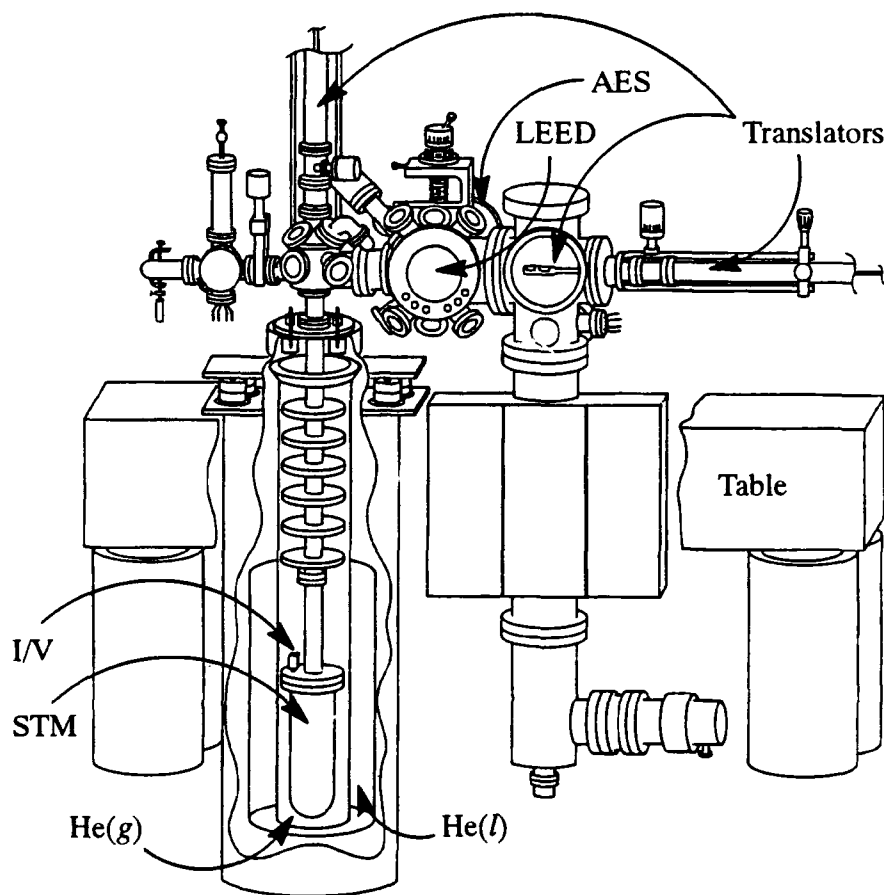


Figure 1. Experimental set up showing the ultrahigh vacuum low temperature scanning tunneling microscope and associated vacuum chambers. The key is as follows: AES - Auger electron spectrometer, He(l) - liquid He dewar, He(g) - exchange gas chamber, I/V - electrometer, LEED - low energy electron diffractometer, STM - low temperature scanning tunneling microscope, Table - custom laser table supporting the instrument, and Translators - vertical and horizontal sample translators.

exchange gas chamber containing *ca.* 1 torr of He gas. The exchange gas chamber is immersed in a liquid He storage dewar with a five day capacity. We have shown using Johnson noise thermometry of the STM tunnel junction that this efficiently cools the STM to the temperature of the liquid He, *i.e.* to $T = 4.5 \pm 0.5 \text{ K}$ [5]. The STM itself is a modified louse design. The room temperature UHV preparation and analysis chamber is equipped with Auger electron spectroscopy, low energy electron diffraction, mass spectroscopy, ion sputtering, multiple sample transport, and rf induction. electron beam, and resistive heating. Samples are dosed by bleeding gas through sapphire leak valves into the upper room temperature chambers with the crystal in one of the upper room temperature chambers or in the microscope at 4K. Of particular importance here is the stability of the low temperature STM which allows us to turn off the feedback loop controlling the STM tip-sample separation for hours at a time and have the tip remain over the same atomic site during this time.

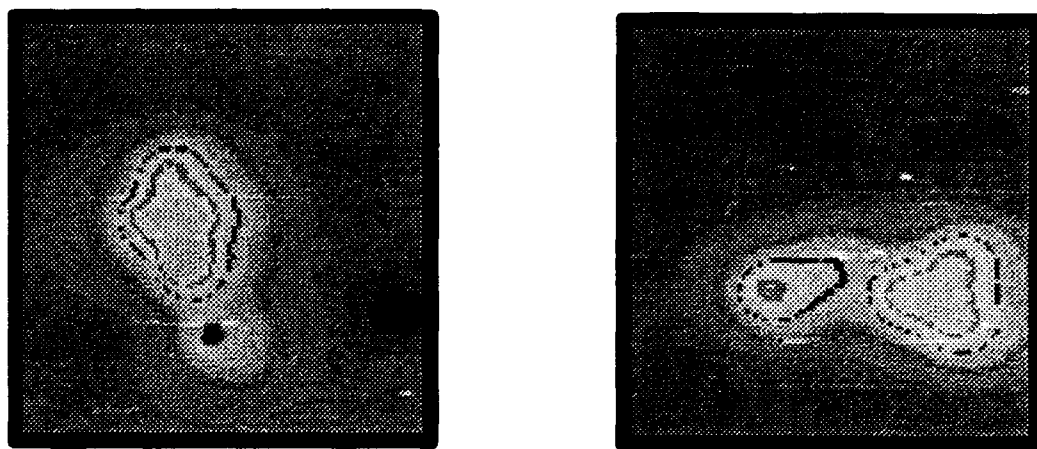


Figure 2. Topographic STM images of a $40\text{\AA} \times 40\text{\AA}$ area showing a cluster of Xe atoms adsorbed on Pt{111} in their initial adsorption site in the left frame, and after moving the cluster to reveal a defect in the right frame. Both images were recorded with a tip bias of ~ 2 mV and a tunneling current of 5 pA. Two gray levels are highlighted to outline the positions of the five Xe atoms.

3. Results

3.1. MOVING XE CLUSTERS

We have found that Xe atoms preferentially bind at step edges on Pt{111} [2]. After these sites are filled, the Xe atoms nucleate into small islands on the Pt{111} terraces. In order to identify the nucleation sites of these islands, we have moved the Xe islands from their initial adsorption sites [2]. Our procedure for moving the islands was:

- 1) Positioning the STM tip over the outer perimeter of the island.
- 2) Turning off the feedback loop.
- 3) Moving the tip in towards the surface by 2.6\AA .
- 4) Changing the tip bias voltage of the tip to $V = \pm 0.010\text{V}$ for 10 msec.
- 5) Returning the bias voltage to its original value (~ 0.002 to ~ 0.010 V).
- 6) Returning the tip to its original height above the surface.

This procedure resulted in centering the island about the STM tip with approximately 50% efficiency [7]. By repeating this procedure, an island could be moved completely away from its initial adsorption site. An example of this is shown in Fig. 2. In all cases when this was done for the Xe islands on the Pt{111} surface, it was found that a depression of $\leq 0.1\text{\AA}$ in the STM images lay underneath the initial island positions. We have tentatively identified these point defects as surface carbon atoms [2]. The concentration of the point defects tracks the surface C contamination as measured by Auger spectroscopy. Theoretical calculations also indicate that a C atom on this surface would appear as a depression in an STM image [6].

3.2. MOVING BENZENE MOLECULES

Benzene adsorbed on Pt{111} appears to exhibit three different types of images depending upon adsorption site [3]. This result is consistent with theoretical calculations of images of benzene on graphite and MoS_2 [9], and the known variety of binding sites for benzene on

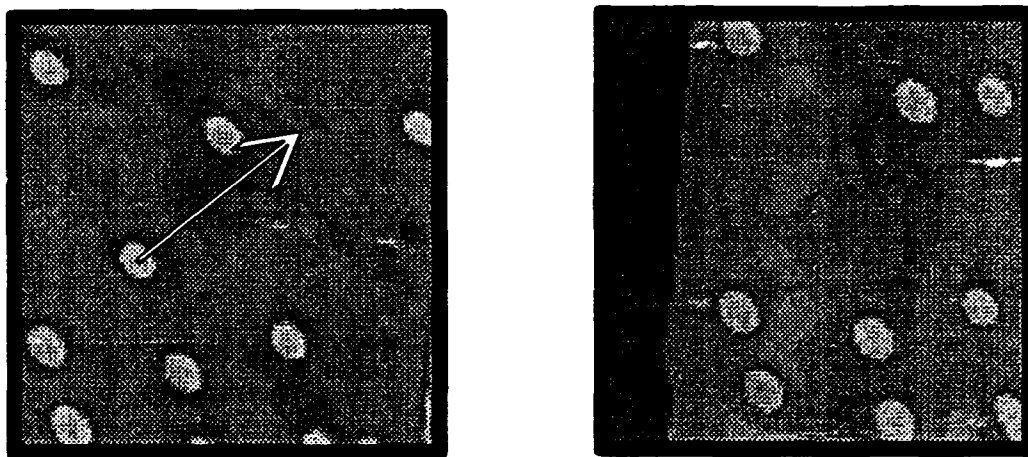


Figure 3. Topographic STM images of a $50\text{\AA} \times 50\text{\AA}$ region of $\text{Pt}\{111\}$ which has been covered with 0.001 monolayers of benzene. Both images were recorded with a tip bias of ~ 10 mV and a tunneling current of 100 pA. Each bump corresponds to a single benzene molecule. The arrow in the left frame indicates the position of a benzene molecule before and after being moved, as described in the text. The right frame shows the surface after the molecule has been moved. Note that the two images are shifted somewhat laterally.

$\text{Pt}\{111\}$ [10,11]. We have used the STM to move benzene from one of these sites to show that benzene which appears simply as a bump for low bias conditions does not sit at a defect. This is shown in Fig. 3. The left panel shows several benzene molecules as imaged initially. Then, one of the benzene molecules was lifted off the surface using the tip and redeposited back on the surface elsewhere (as shown by the arrow in the left panel). The right panel shows both the final position of the benzene molecule which has been moved and the substrate surface at this molecule's adsorption site. There does not appear to be a defect at this site. This is consistent with our interpretation of the different sites which we believe lead to the different images for benzene on this surface [3]. The procedure that we used to lift and replace the molecule was simply shutting off the feedback loop controlling the STM tip-sample separation, moving the STM tip in towards the surface 2.5\AA for 50 msec, then pulling the tip back out and turning the feedback loop on.

While we were able to remove a number of molecules from the surface, this was the only case where we successfully dropped off the molecule afterwards. Still, by attempting to drop off the adsorbate far from the initial adsorption site so as to diminish the possibility of affecting this site, or by imaging with the molecule on the tip, the initial molecular adsorption site can be determined.

4. Conclusions

We have shown how it is both possible and useful to use the scanning tunneling microscope to move adsorbates so as to determine their surface adsorption sites. Knowledge of adsorption sites allows us to understand aspects of film growth and adsorption as well as the STM imaging process itself.

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